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(71) Applicant
Nippon Shokubai Kagaku Kogyo Company Limited (Japan),
5-1 Koraibashi, Higashi-ku, Osaka, Japan

(72) Inventors
Tsuneo Tsubakimoto
Tadao Shimomura
Yoshio Irie

(74) Agent and/or Address for Service
Serjeants,
25 The Crescent, King Street, Leicester

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None

(58) Field of search
C3P

(54) Cross-linked polymers

(57) A method of producing a cross-linked polymer comprises continuously feeding an aqueous solution of a monomer and a polymerization initiator into a vessel 5 provided with parallel rotary stirrer shafts 6, finely dividing a water-containing gel polymer produced by the shearing force of the stirrer blades during solution polymerization, and continuously discharging the resultant finely divided gel polymer. The monomer preferably comprises an α,β-ethlenically unsaturated monomer, such as acrylic acid, methacrylic acid, an alkali metal salt or an ammonium salt thereof, acrylamide or methacrylamide, and a cross-linking monomer possessing at least two polymeric double bonds.

FIG. I

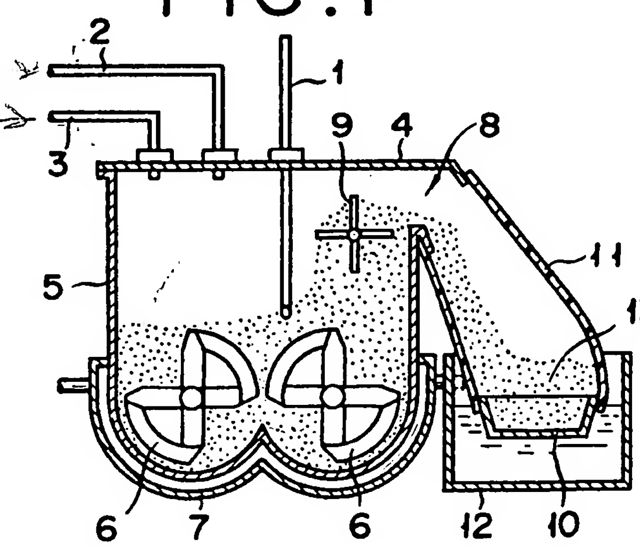

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FIG.1

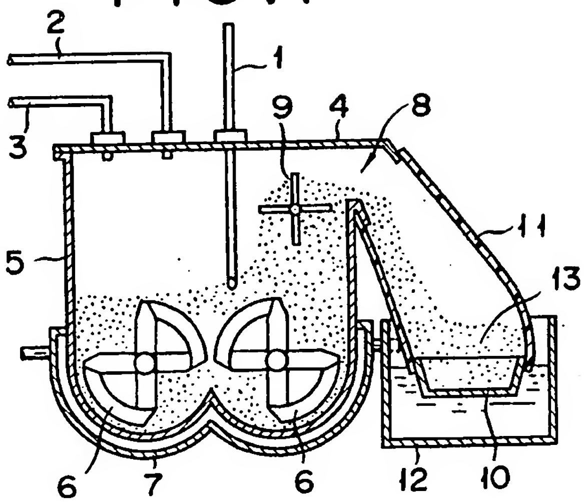


FIG.2

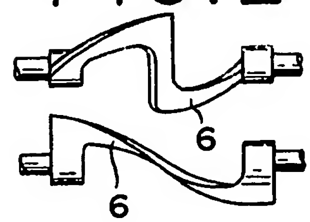


FIG.3

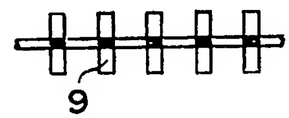


FIG.4

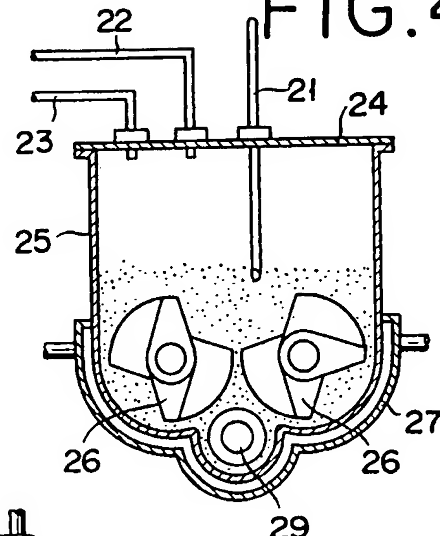
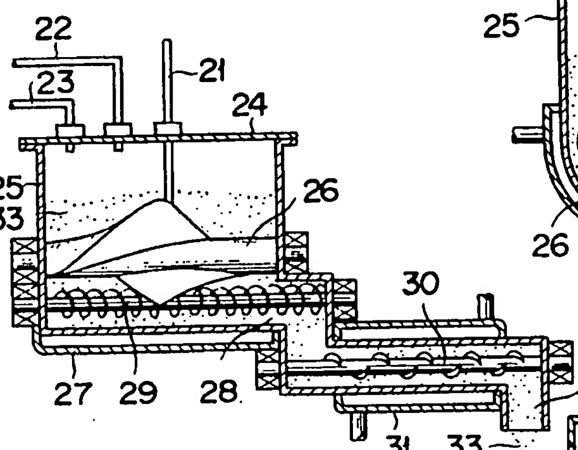


FIG.5



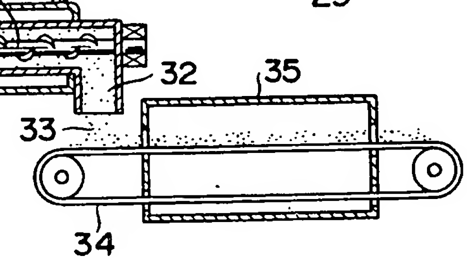


FIG.6(A)

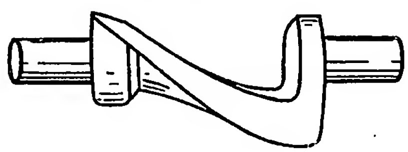


FIG.6(B)

FIG.6(C)

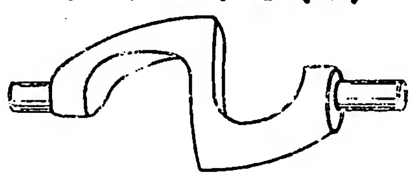


FIG.6(D)

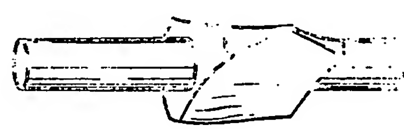
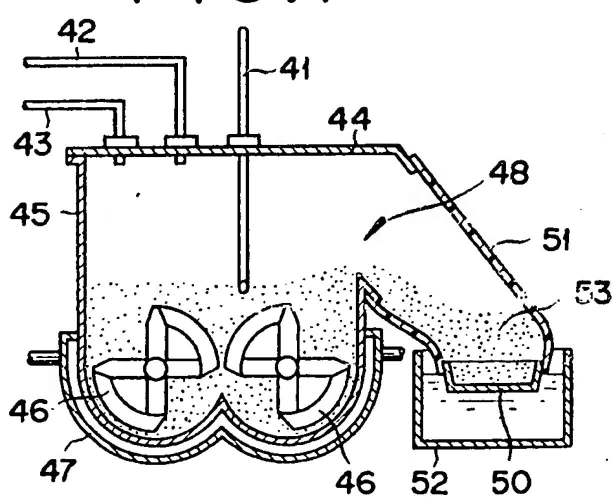


FIG.7



SPECIFICATION

Cross-linked polymers

The invention relates to the production of cross-linked polymers, particularly water-containing gel polymers by aqueous solution polymerization.

Cross-linked polymers of acrylamide, acrylic acid and/or salts thereof have been used for their ability to absorb and retain large volumes of water, effect ion exchange, and induce chelation. They have found extensive utility as sanitary articles, soil conditioners for agronomic uses, dehydration agents, ion-exchange resins and adsorbents. They have been produced by polymerizing an aqueous solution as a water-in-oil emulsion or suspension in a hydrophobic solvent, and by cast polymerizing an aqueous monomer solution. Water-in-oil emulsion polymerization and water-in-oil suspension polymerization entail the use of large volumes or organic solvent and are therefore dangerous. Cast polymerization requires the continual removal of the heat of reaction and so entails intricate and expensive apparatus. Furthermore, producing a cross-linked polymer in a dry state by the removal of water involves finely dividing the polymer to increase its surface area for drying. This may be accomplished by cutting or extrusion, which in either case consumes a huge amount of energy because the polymer has strong rubbery elasticity.

As a solution to these problems, our Patent Specification JP SHO 57(1982)-34101 proposes a method of batchwise radical aqueous solution polymerization in a vessel provided with rotary stirring shafts.

The invention provides a method of producing a cross-linked polymer, which comprises continuously feeding an aqueous solution of a monomer and polymerizing into a water-containing cross-linked gel polymer with a polymerization initiator in a vessel provided with parallel rotary stirrer shafts fitted with blades, finely dividing the gel polymer produced by the shearing force of the stirrer blades during the polymerization, and continuously discharging the resultant finely divided gel polymer from the vessel.

The monomer used should of course be capable of conversion by aqueous solution polymerization into a water-containing cross-linked gel polymer. The cross-linked structure may be that obtainable by the copolymerization of a water-soluble monomer and a cross-linking monomer possessing at least two polymerizable double-bonds in the molecular unit, or by subjecting a water-soluble monomer to aqueous solution polymerization in the presence of a hydrophilic high molecular substance such a starch, cellulose or polyvinyl alcohol and a water soluble poly-epoxide compound so as to effect both polymerization and graft linkage, formation of a complex or ester linkage.

The aqueous monomer solution preferably contains the monomer in a concentration of from 10 to 80% by weight, preferably 20 to 60% by weight. So long as the concentration falls within this range, the water containing gel polymer formed can be easily divided by the shearing force.

Examples of suitable water-soluble monomers include a α,β-ethylenically unsaturated monomers such as acrylic acid and methacrylic acid, alkali metal salts and ammonium salts thereof, acrylamide, methacrylamide, acrylonitrile, 2-hydroxyethyl (meth)acrylate, methyl acrylate, ethyl acrylate, isopropyl acrylate, methyl methacrylate, ethyl methacrylate and maleic acid. A mixture of two or more thereof can be used.

Examples of suitable cross-linking monomers include diacrylate or dimethacrylate of ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, 1,4-butane diol, 1,5-pentane diol, 1,6-hexane diol, neopentyl glycol, trimethylol propane and pentaerythritol; triacrylates of trimethacrylates of trimethylol propane and pentaerythritol; tetracrylates or tetramethacrylates of pentaerythritol, N,N'-methylene-bis-acrylamide, N,N'-methylene-bis-methacrylamide and triallyl isocyanurate. A mixture of two or more thereof can be used. The cross-linking monomer is used generally in the amount of not more than 10 mol%, more desirable 0.0005 to 5 mol%, and most desirably 0.001 to 1 mol%, based on the water-soluble monomer.

A monomer mixture of (A) acrylic acid, methacrylic acid, an alkali metal salt or an ammonium salt thereof, acrylamide or methacrylamide and (B) a cross-linking monomer possessing at least two polymerizable double-bond in the molecular unit is most advantageous. The cross-linking monomer (B) preferably accounts for not more than 10 mol%. Even when the cross-linking monomer (B) is not used at all, the continuous polymerization of the invention can be carried out using of a large amount ammonium persulphate for example as a cross-linking agent.

Examples of vessels suitable for use according to the invention include a two-arm kneader and a three-shaft kneader. The two arms or rotary stirrer shafts are preferably rotated in opposite senses at the same or unequal rates. When the two shafts are operated at equal rates, the radii of rotation of the two shafts partly overlap. When the two shafts are operated at unequal rates, the radii of rotation should not overlap. The stirrer shafts may be of various forms such as sigma, S type, Banbury type or fish tail.

The vessel preferably has its inner surface coated with a fluorine containing plastics material

to prevent adhesion of the gel formed. Examples of suitable materials include tetrafluoroethylene, tetrafluoroethylene-perfluoropropylvinyl ethyl copolymer, tetrafluoroethylene-hexafluoropropylene copolymer, trifluoromonochloroethylene and ethylene-tetrafluoroethylene copolymer.

The vessel is preferably provided in an upper portion with a lid adapted to permit displacement of gas therefrom by an inert gas. The vessel may be provided in an upper part with a reflux condenser for water vapourized by the heat of polymerization. Alternatively, the vessel may be adapted so that the water formed is forced out by a current of an inert gas. For heating and/or partially removing the heat of reaction, it is desirable to provide the polymerization vessel with a jacket. Examples of suitable inert gases include nitrogen, carbon dioxide and argon.

The term "continuous" as used herein should not be interpreted as constant in the exact sense of the word but so as to include the discharge of the polymer in a pulsating manner or in an intermittent manner. The discharge has only to be "continuous" in the sense that the amount of the water-containing gel polymer retained is substantially to a fixed level in the vessel.

Any water-soluble radical polymerization initiator may be used. Examples include persulphates, hydrogen peroxide, and water-soluble azo compounds. They may be used alone or as a redox initiator in combination with a sulphite, a hydrogen sulphite, a thiosulphate, an L-ascorbic acid or a ferrous salt. The amount used may be from 0.001 to 1% by weight, preferably 0.005 to 0.5% by weight, based on the total amount of the reactants.

The reaction temperature is variable with the kind of the monomer to be used. With a monomer mixture of (A) and (B) above, the temperature is generally from 60° to 110°C, preferably from 70° to 100°C. When necessary, the product is subjected to an aging at (to complete its polymerization) from 50° to 120°C, preferably 60° to 100°C.

The particle diameter of the polymer produced depends on the reaction conditions; polymer particles are obtainable in diameters generally not exceeding 3 cm, usually from 0.05 to 1 cm.

Continuous feeding and discharge makes for high operational efficiency and virtually no manual work after the reaction has reached its constant state. The generation of the heat polymerization is uniform because the finely divided gel polymer retained within the vessel and the freshly supplied aqueous monomer solution are uniformly mixed and the polymerization occurs on the surface of polymer gel. Thus, the removal of the heat of the polymerization reaction and the maintenance of the temperature of the polymerization system at a constant level are easy. Consequently, the rate of polymerization can be increased and the productivity of the polymerization can be enhanced, and the maintenance of the product quality at a fixed level is easy to obtain. Polymer obtained has a high absorption capacity and the particles are of substantially uniform diameter and easy to dry.

DRAWINGS

Figure 1 is a schematic cross-section of a reactor suitable for the method of the invention;

Figure 2 is a front view of stirrer blades in the reactor of Fig. 1;

Figure 3 is a side view of a group of discharge blades in the reactor of Fig. 1;

Figure 4 is a schematic cross-section of another reactor suitable for the method of the invention;

Figure 5 is a schematic cross-section of a combination of the reactor of Fig. 4 and a heating device and drier;

Figure 6 is a perspective view of stirrer blades in the reactor of Fig. 4; and

Figure 7 is a schematic cross-section of yet another reactor for the method of the invention.

In Fig. 1, the reactor is a two-arm kneader comprising a vessel 5 provided with a thermometer 1, a raw ~~material feed tube 2~~, an inert gas port 3 and a lid 4. Near the bottom, the kneader is provided with two parallel rotary stirrer shafts 6 each fitted with sigma blades as illustrated in Fig. 2. The vessel contains an atmosphere of inert gas. The vessel 5 is provided at the bottom with a jacket 7 for heat transfer medium to control the reactor temperature. The vessel 5 is also provided near the top with an outlet 8 and with a mechanism for the discharge of finely divided water-containing gel polymer product. The discharge mechanism comprises a horizontal shaft disposed above the stirrer shafts and a number of paddle-like vanes 9. The outlet 8 is connected to a vat 10 by a duct 11 made of plastics material such as polyethylene, polypropylene or polyvinyl chloride. The vat 10 is positioned in a heating bath 12.

Polymerization is effected by feeding aqueous monomer solution containing a water-soluble radical polymerization initiator via the tube 2, at the same time introducing an inert gas such as nitrogen via the ports 3 to displace the air, and maintaining the temperature at a level to induce polymerization. As the polymerization proceeds, the water-containing gel polymer produced is finely divided by the shearing force generated by the rotation of the shaft 6 without interruption of the polymerization. To maintain the amount of gel in the system at a substantially fixed level, particles of the polymer produced are discharged as the polymerization proceeds. The discharged polymer may be heated in the vat 10 to complete its polymerization.

Figs. 4 and 5 show a three-shaft kneader comprising a vessel 25 provided with a thermometer 21, a raw material feed tube 22, an inert gas port 23 and a lid 24. The vessel 25 is provided near the bottom with parallel rotary stirrer shafts 26 having Banbury type blades, and with a discharge screw 29. The vessel contains an atmosphere of inert gas. The vessel 25 is provided at the bottom with a jacket 27 for heat transfer medium to control the reaction temperature. Near the bottom of the vessel 25 is a discharge outlet 28. To the outlet 28 is connected a double-paddle feeder 30 having a jacket 31 and an outlet 32. Below the outlet 32 is a belt conveyor device 34 in a drier 35.

Polymerization is effected by feeding aqueous monomer solution containing a water-soluble radical polymerization initiator via the tube 22, at the same time introducing an inert gas such as nitrogen via the port 23 to displace the air, and keeping the temperature at a level to induce polymerization. As the polymerization proceeds, water-containing gel polymer 33 is produced and finely divided by the shearing force generated by the rotation of the stirrers 26 without interruption of the polymerization. To maintain the amount of gel in the system at a substantially fixed level, it is forced by the discharge screw 29 out of the outlet 28 into the feeder 30. The gel is heated in the feeder 30 to complete its polymerization, discharged through the outlet 32 onto the conveyor 34, and dried by the drier 35.

Fig. 7 illustrates yet another reactor similar to that of Fig. 1, except that a wall on a discharge outlet 48 side of a vessel 45 has a height small enough for the gel produced to leave the vessel 45 by overflowing. The wall 48 is a weir of adjustable height so that it can intermittently be lowered to permit the gel overflow. The reference numerals in Fig. 7 are the same as those in Fig. 1 plus 40, and the polymerization is carried out in the same way.

Example 1

A kneader as illustrated in Fig. 1, has a capacity of 2 litres, a lid 4 opening 160 mm × 150 mm, a depth of 135 mm, and is provided with a two sigma type stirrer blades of 70 mm rotational diameter coated with tetrafluoroethylene-perfluoropropylvinyl ether copolymer on the surfaces exposed to the solution. An aqueous monomer solution containing 399 g of acrylic acid 75 mol% neutralized with caustic soda, 0.036 g of N,N′-methylene-bis-acrylamide, and 600 g of water was fed into the kneader, and nitrogen was blown in to purge oxygen from of the system. The two stirrers were rotated respectively at 67 and 56 r.p.m., water at 45°C was circulated through the jacket 7, and a solution of 0.23 g of 2, 2′-azo-bis-(2-amidinopropane)-dihydrochloride (produced by Wako Junyaku Kabushiki Kaisha and marketed under the designation V-50) in 10 g of water was added as a polymerization initiator. Polymerization began 15 minutes after the addition of the polymerization initiator.

With the progress of the polymerization, the aqueous monomer solution was converted to a soft water-containing gel which was divided finely by the rotation of the stirrers. The temperature of the system reached 80°C within 35 minutes of the addition of the polymerization initiator. At this point, the temperature of the hot water circulating in the jacket 7 was raised to 94°C. An aqueous monomer solution containing 14.36 kg of acrylic acid 75 mol% neutralized with caustic soda, 1.3 g of N,N′-methylene-bis-acrylamide and 21.6 kg of water, purged of oxygen by the passage of nitrogen gas, and a solution of 8.2 g of the initiator V-50 in 360 cc of water were separately fed by constant rate pumps to a mixer tank. The resultant homogenous mixture was fed into the kneader over a period of 24 hours.

The aqueous monomer solution thus fed continuously to the kneader was converted into finely divided water-containing gel polymer, and in that form continuously discharged. The temperature of the system was kept substantially constant at 90°C. The discharged water-containing gel polymer was kept under an atmosphere of nitrogen at 90°C for 20 minutes to complete its polymerization.

The discharged water-containing gel polymer was in the form of finely divided particles from 2 to 7 mm in diameter. The particles lacked cohesiveness, and were easy to handle and to dry. The polymer was spread on a 50 mesh, wire gauze dried in a hot air drier at 150°C, and then pulverized with a vibrating mill. A 0.2 g portion of the pulverized product (hereinafter referred to as "absorbent (1)") was evenly placed in a bag (40 mm × 150 mm) of non-woven fabric shaped like a tea bag, immersed in a 0.9% saline solution for 10 minutes, removed from the water, and weighed. The absorbency of this specimen was calculated in accordance with the following formula, using as a blank an empty bag.

$$\text{Absorbency} = \frac{\text{Weight after absorption} - \text{blank}}{\text{Weight after absorption}}$$

The results shown in Table 1 show the absorbency of the pulverized products from the lots of water-containing gel polymer sampled at intervals of three hours from the start of the continuous supply of the aqueous monomer solution to the polymerization.

TABLE 1

Time elapsed	0	3	6	9	12	15	18	21	24
Absorbency	66	70	72	70	71	71	69	71	71

Thus the polymer obtained is effectively usable as an absorbent.

For visual observation of the behaviour of the aqueous monomer solution continuously added, 5cc of the solution, deaerated and having added thereto 0.2 g of a fluorescent pigment of pink colour (made by the present Applicants and marketed as "Epocolor") and the initiator were added to the system during the continuous polymerization of Example 1. When the coloured monomer solution was added, the entire system assumed a pink colour. This shows that the monomer solution was uniformly mixed with the crushed water-containing gel polymer and had formed a thin coating on the surface of the gel polymer. When the uncoloured monomer solution was added to continue the polymerization, there were produced polymer particles pink at the core and transparent at the outer parts. This shows that the polymer was pulverized in the kneader, and the aqueous monomer solution was deposited on the surface of crushed polymer and underwent polymerization in that state. The particles thus gained in diameter. The grown particles were again pulverized, and the procedure repeated.

Example 2

A kneader constructed as illustrated in Figs. 4 and 5 has a capacity 10 litres, a lid opening 240 mm × 220 mm, a depth of 260 mm, is provided with two Banbury type stirrer blades of 110 mm rotational diameter and a discharge screw 35 mm in diameter, and is coated with trifluoromonochloroethylene resin on the inner surface thereof.

An aqueous monomer solution containing 1995 g of acrylic acid 75 mol% neutralized with caustic soda, 3.3 g of trimethylol propane triacrylate and 3000 g of water was fed into the kneader and nitrogen gas was blown in to purge oxygen from the system. The stirrers were rotated at 30 r.p.m., hot water at 40°C was circulated in the jacket, and 2.25 g of ammonium persulphate and 2.25 g of sodium hydrogen sulphite were added as polymerization initiators. Polymerization began 15 minutes after the addition of the initiators.

With the progress of the polymerization, the aqueous monomer solution was converted into a soft water-containing gel. By the rotation of the stirrers, the gel was divided finely. The temperature of the system rose to 90°C within 25 minutes of the addition of the polymerization initiators. At this point, the temperature of the water circulating in the jacket was raised to 87°C. An aqueous monomer solution containing 359 kg of acrylic acid 75 mol% neutralized with caustic soda, 594 g of trimethylolpropane triacrylate, and 540 kg of water, purged of oxygen by the passage of nitrogen gas, a solution of 405 g of ammonium persulphate in 10 kg of water and a solution of 405 g of sodium hydrogen sulphite in 10 kg of water were supplied to the kneader over a period of 5 days. After the start of the addition of the monomer, the rotation of the discharge screw was controlled so that the amount of the water-containing gel polymer retained in the kneader remained constant.

The aqueous monomer solution continuously fed to the kneader was converted into a finely divided water-containing gel polymer, and in that form continuously discharged. The temperature of the system remained substantially constant at about 83°C.

The water-containing gel polymer discharged was fed into a double paddle feeder (made by Kabushiki Kaisha Nara Kikai Seisakusho) heated by a jacket filled with hot water at 90°C and kept therein for an average residence time of 15 minutes. The polymer discharged from the paddle feeder was dried with a blast of hot air at 160°C in a continuous through-circulation band drier. The dried polymer was sampled at intervals of one half day. Each test specimen was pulverized and the pulverized product (hereafter referred to as "absorbent (2)") was tested for absorbency. The results are shown in Table 2.

TABLE 2

Number of days elapsed	0.5	1	1.5	2	2.5	3	3.5	4	4.5	5
Absorbency	65	66	65	65	65	64	65	66	66	65

Absorbent (2) is an excellent absorbent.

Example 4

The kneader used in Example 1 was modified to the construction of Fig. 7 by cutting a section 150 mm × 50 mm off the upper portion of one wall to allow the overflow of the polymer. An aqueous monomer solution (35% by weight in concentration) containing 250 g of acrylamide, 97 g of potassium acrylate, 3 g of N,N'-methylene-bis-acrylamide and 650 g of

water was fed into the kneader, and nitrogen gas was blown in to purge oxygen from the system. The two sigma type stirrer blades were rotated at respective rates of 44 and 24 r.p.m., hot water at 40°C was circulated in the jacket, and 0.5 g of 35% aqueous hydrogen peroxide solution and 0.006 g of L-ascorbic acid were added as polymerization initiators. Polymerization began one minute after the addition of the initiators.

With the progress of the polymerization, the aqueous monomer solution was converted to a soft water-containing gel. Within 15 minutes of the addition of the polymerization initiators, the temperature of the system reached 64°C. The water-containing gel polymer was divided finely into particles about 3 mm in diameter. At this point, the temperature of the hot water in the jacket was raised to 90°C. An aqueous monomer solution containing 12 kg of acrylamide, 4.66 kg of potassium acrylate, 144 g of N,N'-methylene-bis-acrylamide and 29.2 kg of water, purged of oxygen by the passage of nitrogen gas, a solution of 24 g of a 35% aqueous hydrogen peroxide solution in 1 kg of water, and a solution of 0.288 g of L-ascorbic acid in 1 kg of water were separately fed by constant rate pumps to a mixer tank. The resultant uniform mixture was supplied to the kneader over a period of 24 hours.

The aqueous monomer solution thus continuously fed to the kneader was converted into a finely divided water-containing gel polymer, and in that state was allowed to flow over the wall and leave the kneader continuously. The temperature of the system remained substantially constant at about 85°C. The polymer discharged was kept under an atmosphere of nitrogen at 85°C for 20 minutes to complete its pulverization.

The discharged water-containing gel polymer was in the form of particles divided finely of from about 1 to 5 mm in diameter. The particles lacked cohesiveness, and were easy to handle and to dry. The polymer was spread on a 50 mesh wire gauze and dried with a blast of hot air at 180°C for one hour. The dried product hereinafter referred to as "water-retainer (1)") was in granular form and had a water content of 5% by weight. A 0.5 g portion of the water-retainer (1) was mixed with 100 g of silica sand No. 7. The mixture was spread on a 100 mesh wire gauze, saturated with tap water, left standing at 20°C and 65% RH, and tested for water retaining capacity over a period of time. The change in the amount of water retained by the mixture is shown in Table 3.

TABLE 3

Number of days of standing	0	2	4	6	8
Mixture of water-retainer with sand	80g	51g	36g	20g	15g
Sand alone	30g	9g	1g	0g	0g

The cross-linked polymer is effective as a water retainer.

CLAIMS

1. A method of producing a cross-linked polymer, which comprises continuously feeding an aqueous solution of a monomer and polymerizing into a water-containing cross-linked gel polymer with a polymerization initiator in a vessel provided with a parallel rotary stirrer shafts fitted with blades, finely dividing the gel polymer produced by the shearing force of the stirrer blades during the polymerization, and continuously discharging the resultant finely divided gel polymer from the vessel.

2. A method according to claim 1, wherein the concentration of the monomer in the solution is from 10 to 80% by weight.

3. A method according to claim 1 or claim 2 wherein the vessel is a two-arm kneader.

4. A method according to any preceding claim, wherein the vessel is provided with a discharge screw.

5. A method according to any preceding claim, wherein the gel polymer formed is discharged by the rotation of paddle-shaped vanes disposed near a discharge outlet.

6. A method according to any of claims 1 to 4, wherein the gel polymer formed is discharged by overflow from a weir disposed near a discharge outlet.

7. A method according to any preceding claim, wherein the gel polymer is heated after discharge to complete its polymerization.

8. A method according to any preceding claim, wherein the monomer comprises an α,β-ethylenically unsaturated monomer and not more than 10 mol% of a cross-linking monomer.

9. A method according to any preceding claim, wherein the monomer comprises (A) acrylic acid, methacrylic acid, an alkali metal salt or an ammonium salt thereof, acrylamide or methacrylamide or a mixture of two or more thereof and (B) a cross-linking monomer possessing at least two polymeric double-bonds in the molecular unit.

10. A method according to claim 9, wherein the concentration of the monomer in the solution is from 20 to 60% by weight.

11. A method according to claim 9 or claim 10, wherein the ratio of the cross-linking monomer (B) to the α,β-ethylenically unsaturated monomer (A) is from 0.0005 to 5 mol%.
12. A method according to any preceding claim, wherein the polymerization is carried out from 60° to 110°C.
13. A method of producing a cross-linked polymer as herein described in any of the Examples.
14. A cross-linked polymer produced by a method according to any preceding claim.

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